(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 525 555 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 92112301.4

(22) Date of filing: 18.07.92

(51) Int. Cl.5: C03C 4/08, C03C 3/095, H01J 29/86

(30) Priority: 29.07.91 US 737110

(43) Date of publication of application: 03.02.93 Bulletin 93/05

(84) Designated Contracting States: DE FR GB IT

(71) Applicant: PPG INDUSTRIES, INC.
One PPG Place
Pittsburgh Pennsylvania 15272(US)

(72) Inventor: Jones, James V.
5255 Snowden Drive
Toledo, Ohio 43623(US)

(74) Representative: Sternagel, Hans-Günther, Dr. et al
Patentanwälte Dr. Michael Hann, Dr. H.-G. Sternagel, Dr. H. Dörries, Sander Aue 30
W-5060 Bergisch Gladbach 2(DE)

(54) **X-Ray absorbing glass compositions and cathode ray tube.**

(57) A glass, which is particularly adapted to be melted in conventional glass melting furnaces and formed on a molten tin bath, and which demonstrates exceptional absorption of X-rays with a minimum linear absorption coefficient, measured at 0.6 Angstroms, of 24/cm. and having excellent resistance to electron browning and/or X-ray browning and contains the following components, by weight percent: SiO_2 and Al_2O_3 constituting about 57.0 to 68.0% with SiO_2 constituting about 57.0 to 66.0% and Al_2O_3 constituting about 0 to 5.0%; K_2O and Na_2O constituting about 10.0 to 18.0% with K_2O constituting about 7.0 to 11.0% and Na_2O constituting about 4.0 to 8.0%; BaO and SrO constituting about 16.0 to 24.0% with BaO constituting about 0 to 13.0% and SrO constituting about 11.0 to 21.0%; and CeO_2 constituting about 0.1 to 1.0%, and a cathode ray tube comprising a faceplate formed from such glass.

EP 0 525 555 A1

FIELD OF THE INVENTION

The present invention relates to a glass, which is particularly adapted to be melted in conventional glass melting furnaces and formed on a molten tin bath, and which demonstrates exceptional absorption of X-rays and having good resistance to electron browning and/or X-ray browning.

BACKGROUND OF THE INVENTION

X-radiation is produced when moving electrons are decelerated or stopped due to collisions with the atoms of a substance. The intensity of this X-radiation is function of the accelerating voltage, the electron current, and the atomic number of the material bombarded.

In X-ray tubes, electrons from a hot cathode are focused into a small spot and accelerated to the anode or target. A television picture tube contains the same basic elements as an X-ray tube, that is a focused beam of electrons and a high D.C. accelerating voltage.

In computer monitor and color television picture tube applications, higher voltages are employed than in "black and white" applications, making X-ray emission absorption a very important consideration, particularly in the area of the glass tube face plate.

The prior art is replete with glass compositions directed to the absorption of X-rays, as for example U.S. Patent Nos. 3,464,932, 4,015,966, 4,065,696, 4,065,697. Many of the glass compositions disclosed in the prior art may adequately absorb X-ray emissions but contain certain levels of materials that significantly interfere with the "standard" glass manufacturing processes.

The glass composition should be compatible with the refractories used in the glass melting and forming apparatus such that it does not cause the refractories to dissolve at an accelerated rate during glass melting and forming. In addition, the glass composition should not contain materials which will volatilize during glass melting and forming, since this will damage the refractory superstructures and also cause emissions of noxious odors and gases.

If the conventional molten tin float glass forming process is employed, as disclosed in U.S. Patent Nos. 3,220,816 and 3,843,346, the glass composition should be compatible with the molten tin and should not contain any easily reducible oxides which will cause a film to form on the glass at the tin/glass interface. An easily reducible oxide will also tend to contaminate the tin bath with undesirable materials which may cause flaws in subsequently formed glass.

While certain of the prior art X-ray absorbing glass compositions have satisfied several of these important problems, none of these glass compositions have provided a glass which is particularly adapted to be manufactured by conventional float glass melting and forming processes and equipment and which demonstrates exceptional absorption of X-rays.

SUMMARY OF THE INVENTION

The present invention provides a glass which is particularly adapted to be manufactured by conventional glass melting and forming processing and equipment and which demonstrates exceptional absorption of X-rays and more particularly, provides a minimum linear absorption coefficient, measured at 0.6 Angstroms, of 24/cm. of glass thickness. The glass also provides good resistance to electron browning and X-ray browning. In one particular embodiment of the invention, the glass composition includes SiO_2 and Al_2O_3 combining to constitute about 57.0 to 68.0 weight percent of the glass composition with SiO_2 constituting about 57.0 to 66.0 weight percent and Al_2O_3 constituting about 0 to 5.0 weight percent; K_2O and Na_2O combining to constitute about 10.0 to 18.0 weight percent of the glass composition with K_2O constituting about 7.0 to 11.0 weight percent and Na_2O constituting about 4.0 to 8.0 weight percent; BaO and SrO combining to constitute about 16.0 to 24.0 weight percent of the glass composition with BaO constituting about 0 to 13.0 weight percent and SrO constituting about 11.0 to 21.0 weight percent; and CeO_2 constituting about 0.1 to 1.0 weight percent of the glass composition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph showing the relationship of network formers to total alkalis and its effect on the glass expansion coefficient.

FIGURE 2 is a graph showing the relationship of network formers to the glass expansion coefficient.

FIGURE 3 is a graph showing the relationship of strontium oxide to barium oxide and its effect on the glass liquidus temperature.

FIGURE 4 is a graph showing the relationship of strontium oxide to sodium oxide and its effect on the glass liquidus temperature.

FIGURE 5 is a graph showing the relationship of silicon dioxide to strontium oxide and its effect on the glass liquidus temperature.

FIGURE 6 is a graph showing the relationship of silicon dioxide to barium oxide and its effect on the glass liquidus temperature.

FIGURE 7 is a graph showing the change of the sum of alkaline earths (i.e. SrO + BaO + CaO + MgO) and their effect on the glass density.

FIGURE 8 is a graph showing the relationship of sodium oxide to potassium oxide and its effect on the glass density.

FIGURE 9 is a graph showing the relationship of strontium oxide to barium oxide and its effect on the glass strain point.

DETAILED DESCRIPTION OF THE INVENTION

The process of making glass is energy intensive requiring the expenditure of considerable energy to make a final product free of defects. It is, therefore, highly desirable that the glass composition, of the type generally contemplated by this invention, be relatively easy to melt with a log ten viscosity = 2.0 of less than 2650 °F (1460 °C). The method used to measure the temperatures for the range of log ten viscosity = 2.0 to 6.0 is in accordance with American Society for Testing Material (ASTM) Method C 965-81.

It is also desirable that the glass composition have a positive working range which is defined as the difference between its temperature at log ten viscosity = 4.0 and the liquidus temperature. The liquidus temperature is defined as the temperature at which the first crystal forms when cooling or where crystals first dissolve when heating. ASTM Method C 829-81 is one method of measuring the liquidus temperature.

When glass is used as a face plate on a cathode ray tube (CRT), the glass properties of expansion coefficient and strain point are critical because the face plate must be fused to the funnel part of the CRT. The CRT is thereafter sealed and a vacuum is applied to the interior of the assembled tube which creates a strain on the overall glass tube structure. The fused area between the face plate and the funnel is an area where the strains are generally higher than at any other portion of the glass tube structure. Therefore, both the expansion coefficient and the strain point of the face plate must closely match the both the expansion coefficient and the strain point of the funnel tube to prevent stress build-up in the common area or junction where both glass compositions are fused together. ASTM Method E 228-71 is a method of measuring the expansion coefficient and ASTM Method C 336-71 is a method of measuring the annealing range and the strain point.

The above-described desirable glass properties are all evidenced by the glass of the present invention and several examples of the recorded numerical values of these properties are as set forth in some detail below in the description of this invention.

It is also very important that glass compositions not dissolve the refractories where there is glass contact during melting nor should the glass contain materials which may volatilize and react with the refractories used in the head space within the glass melting apparatus. ASTM Method C 621-68 is a method of testing the corrosion resistance of refractories.

The glass of the present invention is less corrosive to refractories than typical prior art X-ray absorbing glasses and particularly less corrosive than glass adapted to be formed using the float glass forming process. The float glass forming process is a well known prior art process and is described in U.S. Patent Nos. 3,220,816 and 3,843,346.

The following Table 1 indicates the difference in metal line cuts in a 48 hour test with typical soda-lime-silica float glass (denoted as "A") and the glass of the present invention (denoted as "B") relative to the refractories used in glass making furnaces based on ASTM Method C 621-68 testing.

An example of a composition (by weight percent) of a typical soda-lime-silica glass formed by the float glass forming process and used in Table 1 below, is as follows:

SiO_2	73.07	SO_3	0.24
Na_2O	13.77	Fe_2O_3	0.088
K_2O	0.04	Al_2O_3	0.12
MgO	3.84	SrO	0.007
ZrO_2	0.009	CaO	8.81

TABLE 1

METAL LINE CUTS OF GLASS ON REFRACTORIES

GLASS COMPOSITION (cm.)	REFRACTORY*	TEMP. (°C)	METAL LINE CUT
A (Prior Art)	MONOFRAX S3	1454	0.081
B (Present Invention)	MONOFRAX S3	1454	0.043
A	MONOFRAX S3	1510	0.208
B	MONOFRAX S3	1510	0.066
A	MONOFRAX M	1454	0.226
B	MONOFRAX M	1454	0.079
A	MONOFRAX M	1510	0.396
B	MONOFRAX M	1510	0.262
A	MONOFRAX Z	1454	0.109
B	MONOFRAX Z	1454	0.097
A	MONOFRAX Z	1510	0.417
B	MONOFRAX Z	1510	0.302

* Each of the refractories listed in the above Table 1 are as manufactured by the Carborundum Corporation of Niagara, New York under the above noted trade designations.

When glass is exposed to high voltage X-rays, as for example the glass face plate in color television picture tube applications, most prior art glass compositions will become discolored or "brown". It is, therefore, highly desirable that the glass composition contain a material which prevents the browning to maintain a high degree of light transmission. Cerium oxide performs this function in the composition of the present invention very well.

In order to form glass compositions using a molten tin float glass forming process, the glass should not contain any materials which will strongly reduce the tin. If the tin becomes reduced by one or several glass components, a tin film will form on the bottom surface of the formed glass which will severely limit the light transmission through the glass. Also any such undesirable component in the glass would likely diffuse into the molten tin bath causing the tin bath to be "poisoned" and result in defects in subsequent glass compositions formed on the same bath. An example of such an undesirable glass component as found in

certain prior art glass compositions is lead oxide. Lead oxide has been commonly used in some X-ray absorbing glass compositions because it readily absorbs X-rays.

There are six components necessary to meet the above described requirements of an X-ray absorbing glass composition which can be melted in a conventional glass-making furnace and that can be formed on a molten tin bath. The six commonly used batch components are: sand, soda ash, potassium carbonate, barium carbonate, strontium carbonate and cerium carbonate. Other batch materials may be used as long as they contain the necessary oxides as listed below. The resultant glass product then contains the following essential oxides: silicon dioxide (SiO_2), sodium oxide (Na_2O), potassium oxide (K_2O), barium oxide (BaO), strontium oxide (SrO) and cerium oxide (CeO_2).

Since other glass compositions may be melted in a particular tank prior to the melting of the glass of the present invention, the final product may contain remnants of the previously melted glass compositions and/or minute amounts of dissolved refractories from the glass furnace. The glass of the present invention may also contain small amounts of components normally used to color glass in order to provide a desired light transmission, although colorants are not an essential element to the present invention.

Therefore, glass of this invention contains less than 2% of colorants, dissolved refractories, tramp components from batch materials, or remnants of compositions previously melted in the furnace. None of these 2% or less components are essential to meet the requirements of this invention nor would they generally adversely affect the desired properties of the glass of this invention.

The function of SiO_2 in this glass composition is to act as a network former and provide the basic structure of a glassy matrix. Other minor network formers in glasses of this invention include alumina oxide (Al_2O_3), sulfur trioxide (SO_3) and cerium oxide (CeO_2).

Na_2O and K_2O are alkalis used in glass compositions of this invention to aid in melting the glass and to adjust the expansion coefficient of the composition.

Several of the above described highly desirable physical properties of the glass of this invention are as shown in FIGURES 1 to 9.

The expansion coefficient, which is depicted in FIGURES 1 and 2, is a critical physical property in that there must be a close expansion "match" between the face plate glass and the funnel glass of a cathode ray tube, the former being sealingly fused to the latter. The expansion coefficient of the glass of this invention can be so adjusted to match the range of expansion coefficients of the typical funnel glasses to ensure an efficient and effective fusion therebetween.

FIGURE 1 is a graph which shows that when the ratio of network formers to total alkalis is lowered the expansion coefficient increases.

FIGURE 2 is a graph which also shows that when the total of network formers is lowered the expansion coefficient increases.

The liquidus temperature which is depicted in FIGURES 3 to 6, is also a critical physical property in that it is essential to maintain a low liquidus temperature. Low liquidus temperatures permit glass forming without concern from spontaneous crystallization which adversely affects all types of glass forming operations.

FIGURE 3 is a graph which shows that as the ratio SrO to BaO decreases, the liquidus temperature is lowered. Both SrO and BaO function as major absorbers of X-rays in the glass of this invention. SrO is relatively a better X-ray absorber than BaO, but BaO is essential to maintain a low liquidus temperature for the glass of this invention.

FIGURE 4 is a graph which shows that the liquidus temperature is lowered when the ratio of SrO to Na_2O is decreased.

FIGURE 5 is a graph which shows that increasing the ratio between SiO_2 and SrO will also decrease the liquidus temperature.

FIGURE 6 is a graph which shows that when the SiO_2 to BaO ratio is below 15 then the liquidus temperature will be below 1016 °C (1850 °F).

The glass density, which is depicted in FIGURES 7 and 8, is also a critical physical property in that it enhances the X-ray absorption properties of the glass. The mass X-ray absorption coefficient is calculated at 0.6 Angstroms by the method described on page 20, Table 5 in Electronic Industries Association (EIA) publication No. TEP-194, prepared by EIA Tube Engineering Panel Advisory Council.

FIGURE 7 is a graph which shows that as the concentration of the alkaline earths (i.e. SrO + BaO + CaO + MgO) increases, the glass density increases.

FIGURE 8 is a graph which also shows that as the ratio between Na_2O and K_2O decreases the glass density increases.

The strain point, which is depicted in FIGURE 9, is also a another critical physical property. A low strain point becomes very important when fusing a face plate of a CRT to the funnel. The fusing of these tube

parts should be accomplished without generating any stresses in the area of the fusing junction.

FIGURE 9 is a graph which shows that as the ratio between SrO and BaO decreases the strain point is lowered.

As before indicated, CeO_2 is a good X-ray absorber and performs that function in the glass composition of the present invention as well as the primary function of preventing X-ray browning. As above described, X-ray browning lowers the light transmission quality of the glass and typically occurs when the glass is exposed to a high voltage electron source which emits X-rays.

Table 2 below records a number of glass compositions expressed in terms of parts by weight on the oxide basis, illustrating parameters of the present invention. Because the sum of the individual components closely approximates 100, for all practical purposes the tabulated values may be considered to represent weight percent. The ingredients actually making up the batch for each glass may comprise any materials, either oxides or other compounds, which when melted together, will be converted into the desired oxides in the proper proportions. As before indicated, glasses of this invention may contain other minor network formers including Al_2O_3, SO_3 and CeO_2. As also before indicated, glass of this invention may contain colorants, fining agents, dissolved refractories, tramp components from batch materials, or remnants of compositions previously melted in the furnace. More particularly, the batch may include colorants, such as but not limited to, NiO, CoO, Se and Fe_2O_3 and fining agents, such as but not limited to, Na_2SO_4 and CaF_2. These materials account for up to 2 weight percent and preferably less than 1 weight percent of the batch composition. Similarly, dissolved refractory, such as but not limited to, ZrO_2, tramp material, such as but not limited to, TiO_2, and remnant materials, such as but not limited to, CaO and MgO account for up to 1 weight percent and preferably less than 0.5 weight percent of the batch composition.

Table 3 reports measurements of physical properties carried out on the specimens using the above indicated testing methods.

TABLE 2

OXIDE	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7	EXAMPLE 8
SiO_2	57.79	65.20	59.63	59.97	63.85	65.48	64.00	64.40
Na_2O	6.43	7.04	6.64	4.78	6.60	6.80	7.00	6.16
K_2O	8.06	8.83	8.33	10.46	9.00	7.50	7.50	8.52
SrO	11.29	20.55	17.59	11.73	12.00	15.00	13.00	11.36
BaO	11.96	0.00	2.45	12.43	7.90	2.42	7.75	7.10
Al_2O_3	1.89	0.00	4.73	0.00	0.00	2.00	0.00	1.86
CeO_2	0.13	0.28	0.53	0.53	0.50	0.50	0.50	0.50

TABLE 3

PROP.	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7	EXAMPLE 8
STRAIN POINT IN °C								
	491	492	507	490	463	491	469	479
DENSITY AT 20°C IN GRAMS/CC.								
	2.824	2.756	2.714	2.871	2.739	2.661	2.756	2.695
EXPANSION COEFFICIENT (x 10-6/°C) FROM 25-300°C								
	10.57	10.66	10.28	11.01	10.08	9.52	10.95	9.97
24 HOUR LIQUIDUS TEMPERATURE IN °C								
	985	1075	1116	938	890	999	877	873
LINEAR ABSORPTION COEFFICIENT (PER CM OF GLASS THICKNESS)								
	32.2	36.9	33.8	34.1	29.7	29.5	31.1	27.9

The glass compositions of Table 2 were prepared as follows:

(a) The batch components were weighed on a laboratory balance scale and then mixed in a V-shaped blender for approximately ten minutes.

(b) Approximately 1.5 pounds (0.68 kg) of the mixed batch components were melted in a four-inch diameter, four-inch high (10.2 cm by 10.2 cm) platinum/rhodium crucible for two hours at 2550°F

(1399 °C).

(c) The glass was then fritted by pouring it carefully into a container cooled by running water. The glass was thereby shattered and thereafter the water was drained and the glass was returned to a crucible.

(d) The fritted glass was melted for four hours at 2700 °F (1482 °C).

(e) The glass was poured on a steel casting table and rolled to a nominal thickness of 0.25 inch (0.64 cm) thickness.

(f) The glass was annealed in a lehr from a temperature of 1200 °F (649 °C). The glass was slowly cooled for approximately sixteen hours. The glass was then cut into sample segments.

The glass sample segments were then ready for the tests using the above referred to testing techniques.

It was observed that the total amount of network formers and alkalis each affected the coefficient of linear expansion of the glass samples but in opposite ways. More particularly, as the total amount of network formers increased, the expansion coefficient dropped. Conversely, as the total amount of alkalis increased, the expansion coefficient increased. As a result, although not limiting in the present invention, in a preferred embodiment of the invention, the network formers in the form of SiO_2 and Al_2O_3 combined to constitute between about 57 to 68 weight percent of the glass batch, with the SiO_2 constituting about 57 to 66 weight percent and the Al_2O_3 constituting about 0 to 5 weight percent. In addition, the alkalis in the form of K_2O and Na_2O combined to constitute between about 10 to 28 weight percent, with K_2O constituting about 7 to 11 weight percent and Na_2O constituting about 4 to 8 weight percent. In a more preferred embodiment of the invention, the SiO_2 and Al_2O_3 combined to constitute about 61 to 67 weight percent, with the SiO_2 constituting about 61 to 66 weight percent and the Al_2O_3 constituting about 0 to 3 weight percent, and the K_2O and Na_2O combined to constitute between 14 to 17 weight percent of the glass batch, with the K_2O constituting about 7.5 to 9.5 weight percent and the Na_2O constituting about 6.5 to 7.5 weight percent.

It was further observed that as the amount of BaO and SrO increased, the liquidus temperature of the glass batch increased resulting in defects forming in the glass which would cause the glass to break as it cooled. As a result, although not limiting in the present invention, it is preferred that the BaO and SrO combine to constitute between 16 to 24 weight percent of the glass batch, with BaO constituting about 0 to 13 weight percent and SrO constituting about 11 to 21 weight percent. Furthermore, it is more preferable that the BaO and SrO combine to constitute about 17 to 22 weight percent of the glass batch, with the BaO constituting about 3 to 8 weight percent and the SrO constituting about 11.5 to 15 weight percent.

As can be adjudged from the above Tables 2 and 3 and the previous discussion of the present invention, a glass composition within the ranges of the claimed invention exhibits the desired properties, including the desired melting and forming behavior and physical properties.

Claims

1. A glass demonstrating exceptional absorption of X-rays with a minimum linear absorption coefficient, measured at 0.6 Angstroms, of 24/cm. of glass thickness and having excellent resistance to electron browning and/or X-ray browning and containing the following components, by weight percent: SiO_2 constituting about 57.0 to 66.0%; Al_2O_3 constituting about 0 to 5.0%; K_2O constituting about 7.0 to 11.0%; Na_2O constituting about 4.0 to 8.0%; BaO constituting about 0 to 13.0%; SrO constituting about 11.0 to 21.0%; and CeO_2 constituting about 0.1 to 1.0%.

2. A glass demonstrating exceptional absorption of X-rays of claim 1 wherein SiO_2 constitutes about 61.0 to 66.0%; Al_2O_3 constitutes about 0 to 3.0%; K_2O constitutes about 7.5 to 9.5%; Na_2O constitutes about 6.5 to 7.5%; BaO constitutes about 3.0 to 8.0%; SrO constitutes about 11.5 to 15.0%; and CeO_2 constitutes about 0.2 to 0.6%.

3. A glass demonstrating exceptional absorption of X-rays of claim 1 wherein SiO_2 and Al_2O_3 constitute about 57.0 to 68.0%; K_2O and Na_2O constitute about 10.0 to 18.0%; BaO and SrO constitute about 16.0 to 24.0%; and CeO_2 constitutes about 0.1 to 1.0%.

4. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein SiO_2 and Al_2O_3 constitute about 61.0 to 67.0%.

5. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein K_2O and Na_2O constitute about 14.0 to 17.0%.

6. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein BaO and SrO constitute about 17.0 to 22.0%.

7. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein CeO_2 constitutes about 0.2 to 0.6%.

8. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein SiO_2 and Al_2O_3 constitute about 61.0 to 67.0% with SiO_2 constituting about 61.0 to 66.0% and Al_2O_3 constituting about 0 to 3.0%.

9. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein K_2O and Na_2O constitute about 14.0 to 17.0% with K_2O constituting about 7.5 to 9.5% and Na_2O constituting about 6.5 to 7.5%.

10. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein BaO and SrO constitute about 17.0 to 22.0% with BaO constituting about 3.0 to 8.0% and SrO constituting about 11.5 to 15.0%.

11. A glass demonstrating exceptional absorption of X-rays of claim 3 wherein SiO_2 and Al_2O_3 constitute about 61.0 to 67.0% with SiO_2 constituting about 61.0 to 66.0% and Al_2O_3 constituting about 0 to 3.0%; K_2O and Na_2O constitute about 14.0 to 17.0% with K_2O constituting about 7.5 to 9.5% and Na_2O constituting about 6.5 to 7.5%; BaO and SrO constitute about 17.0 to 22.0% with BaO constituting about 3.0 to 8.0% and SrO constituting about 11.5 to 15.0% and CeO_2 constitutes about 0.2 to 0.6%.

12. A glass demonstrating exceptional absorption of X-rays of claim 1 wherein said glass further contains dissolved refractories, tramp components from batch materials and remnants of previously melted glass batches in an amount not to exceed 1% by weight percent of the total glass weight.

13. A glass demonstrating exceptional absorption of X-rays of claim 1 wherein said glass further contains fining agents and colorants in an amount not to exceed 2% by weight percent of the total glass weight.

14. A glass demonstrating exceptional absorption of X-rays of claim 1 wherein said glass is formed by a molten tin float process.

15. A cathode ray tube comprising a glass funnel portion, a glass faceplate sealingly fused thereto, an electron gun disposed within said cathode ray tube, said electron gun emitting high voltage X-rays, at least said faceplate being formed from a glass demonstrating exceptional absorption of X-rays with a minimum linear absorption coefficient, measured at 0.6 Angstroms, of 24/cm. of glass thickness and having excellent resistance to electron browning and/or X-ray browning and containing the following components, by weight percent: SiO_2 constituting about 57.0 to 66.0%; Al_2O_3 constituting about 0 to 5.0%; K_2O constituting about 7.0 to 11.0%; Na_2O constituting about 4.0 to 8.0%; BaO constituting about 0 to 13.0%; SrO constituting about 11.0 to 21.0%; and CeO_2 constituting about 0.1 to 1.0%.

16. A glass demonstrating exceptional absorption of X-rays of claim 15 wherein SiO_2 constitutes about 61.0 to 66.0%; Al_2O_3 constitutes about 0 to 3.0; K_2O constitutes about 7.5 to 9.5%; Na_2O constitutes about 6.5 to 7.5%; BaO constitutes about 3.0 to 8.0%; SrO constitutes about 11.5 to 15.0%; and CeO_2 constitutes about 0.2 to 0.6%.

17. A glass demonstrating exceptional absorption of X-rays of claim 15 wherein SiO_2 and Al_2O_3 constitute about 57.0 to 68.0%; Na_2O and K_2O constitute about 10.0 to 18.0%; and BaO and SrO constitute about 16.0 to 24.0%.

18. A glass demonstrating exceptional absorption of X-rays of claim 17 wherein SiO_2 and Al_2O_3 constitute about 61.0 to 67.0%; Na_2O and K_2O constitute about 14.0 to 17.0%; BaO and SrO constitute about 17.0 to 22.0%; CeO_2 constitutes about 0.2 to 0.6%.

19. A glass demonstrating exceptional absorption of X-rays of claim 17 wherein SiO_2 and Al_2O_3 constitute about 61.0 to 67.0% with SiO_2 constituting about 61.0 to 66.0% and Al_2O_3 constituting about 0 to 3.0%; K_2O and Na_2O constitute about 14.0 to 17.0% with K_2O constituting about 7.5 to 9.5% and Na_2O constituting about 6.5 to 7.5%; BaO and SrO constitute about 17.0 to 22.0% with BaO constituting about 3.0 to 8.0% and SrO constituting about 11.5 to 15.0%; and CeO_2 constitutes about 0.2 to 0.6%.

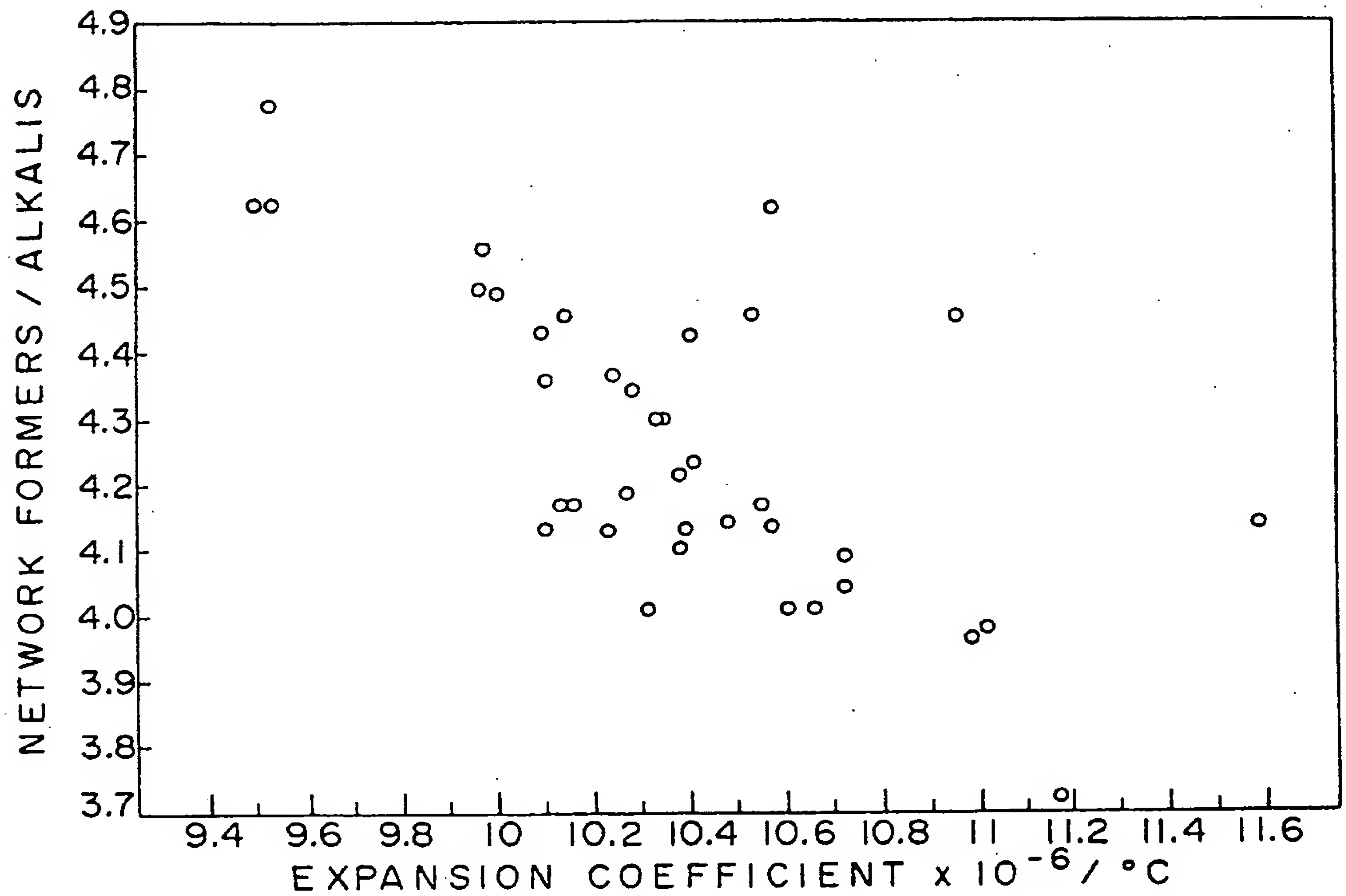


FIG.1 - LOWER NETWORK / ALKALI RAISES EXPANSION

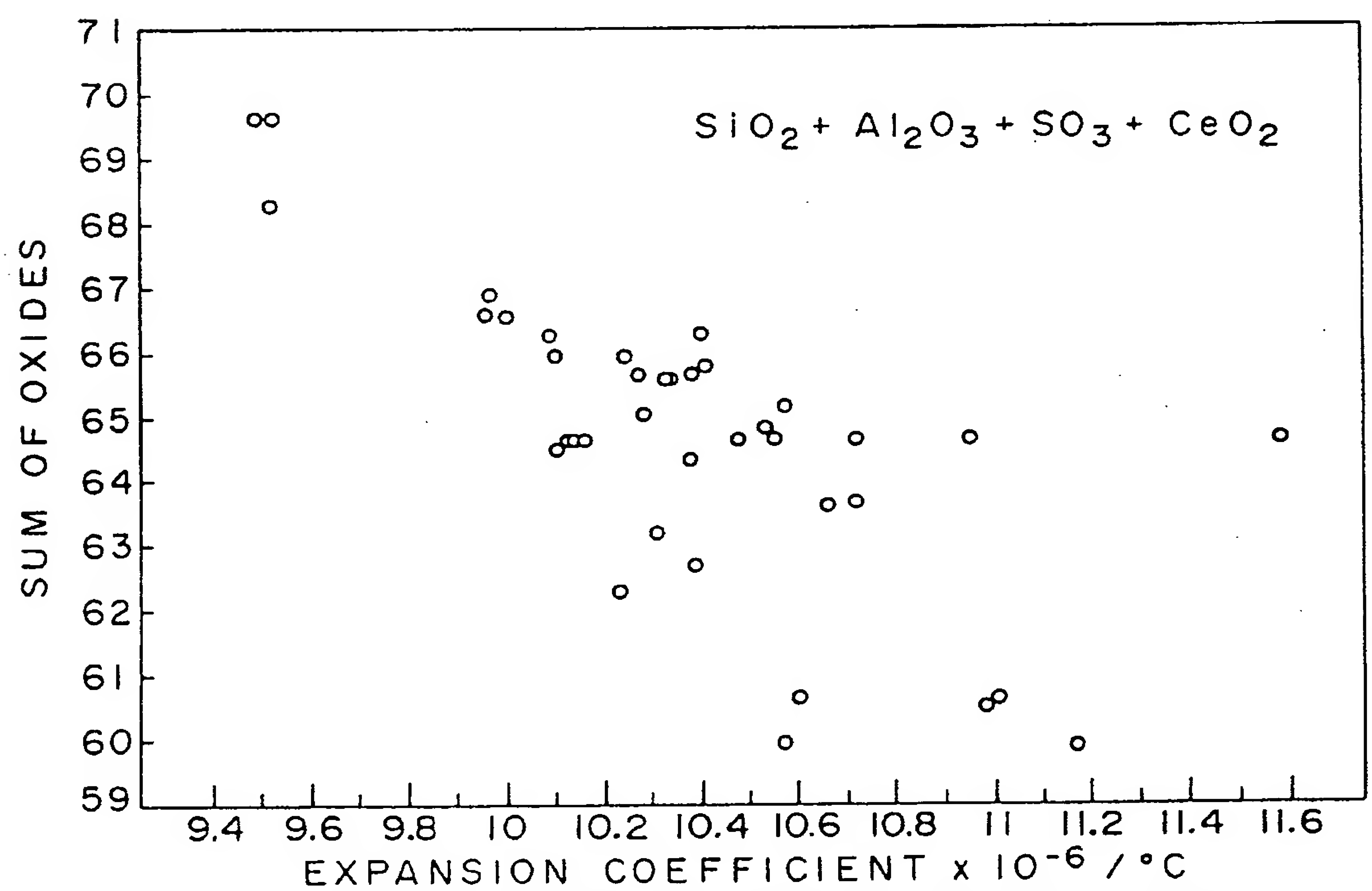


FIG. 2 - DECREASES NETWORK RAISES EXPANSION

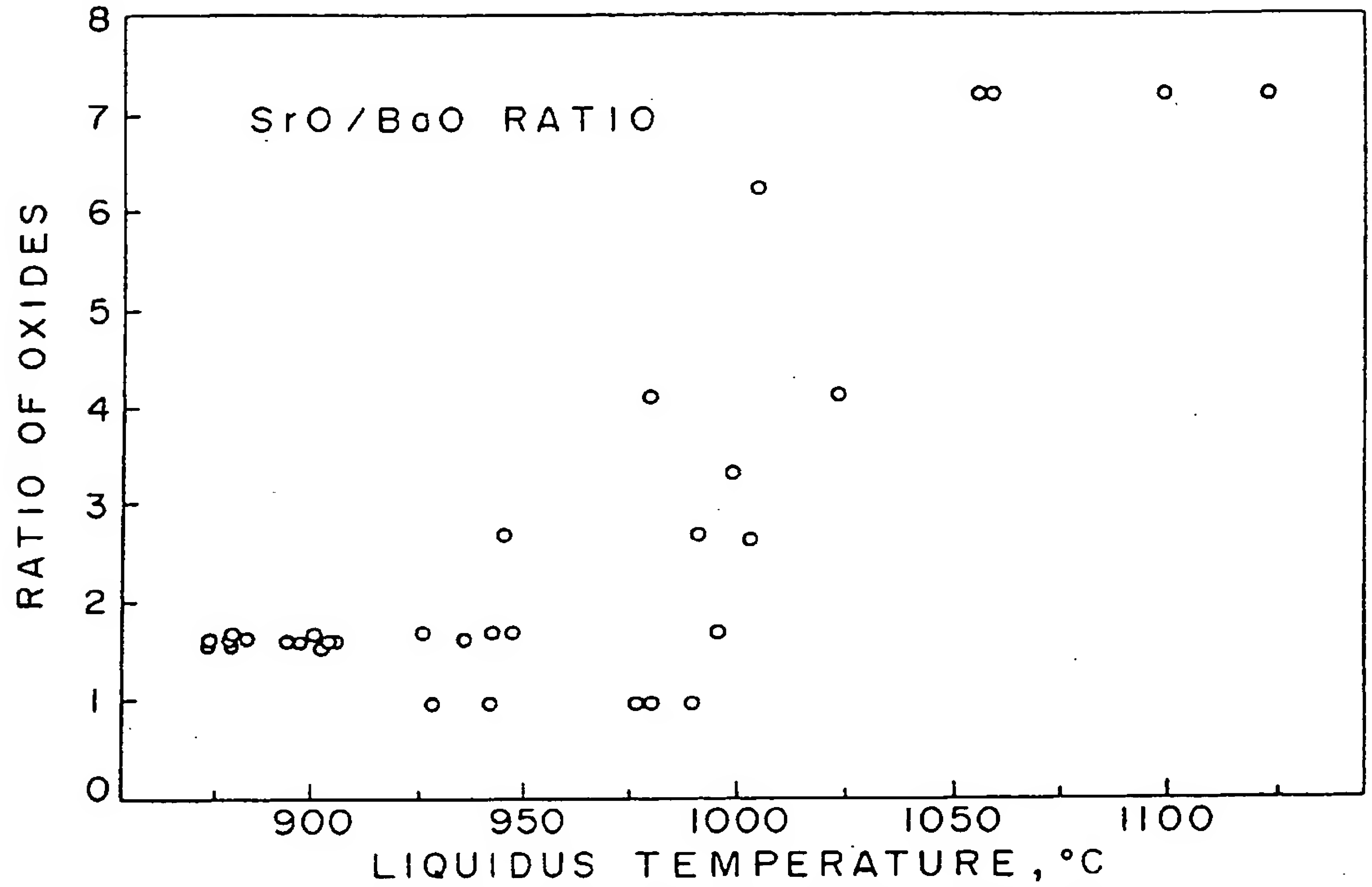


FIG.3-DECREASE SrO/BaO RATIO LOWERS LIQUIDUS

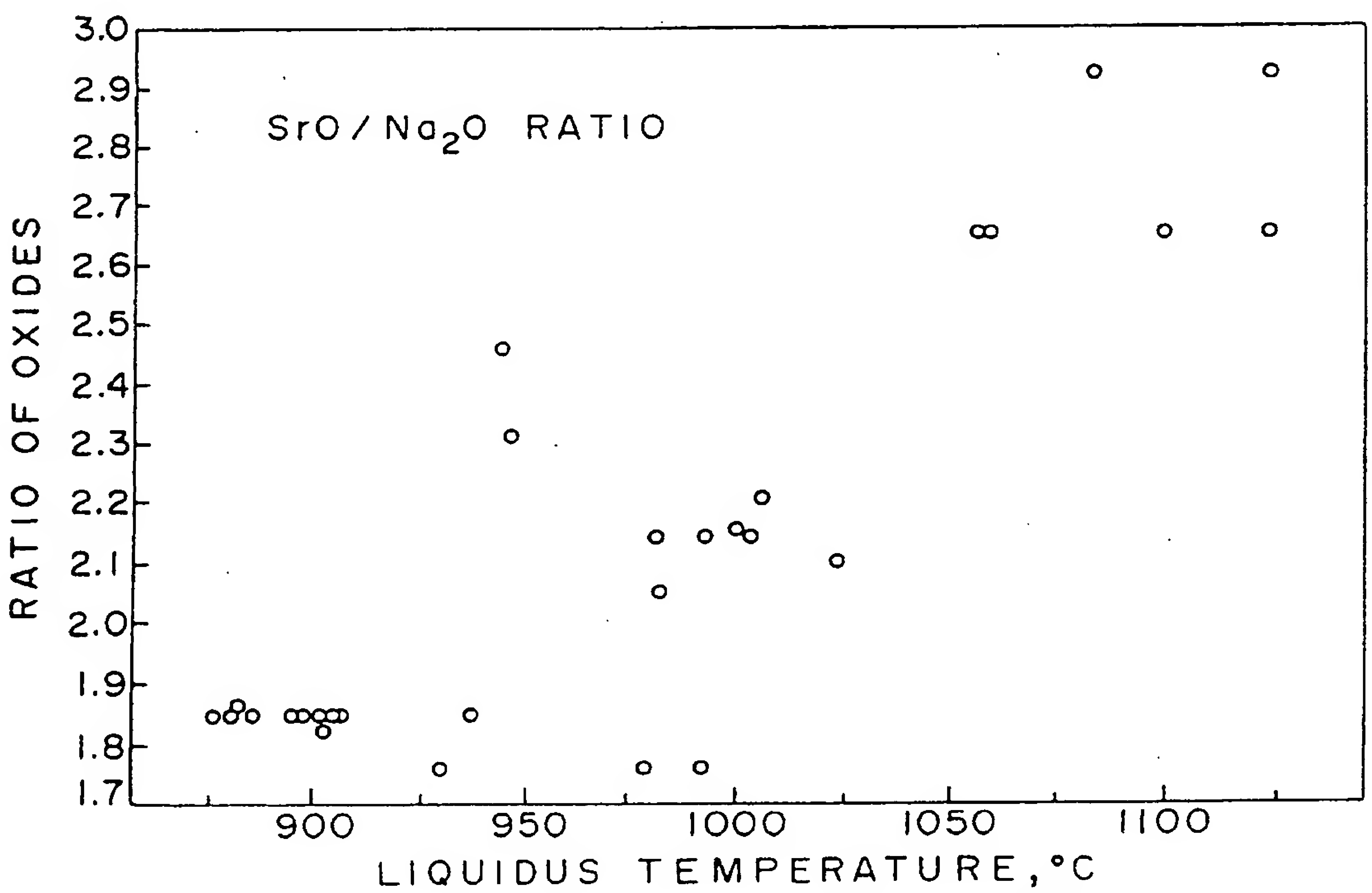


FIG. 4 - DECREASE SrO/Na_2O RATIO LOWERS LIQUIDUS

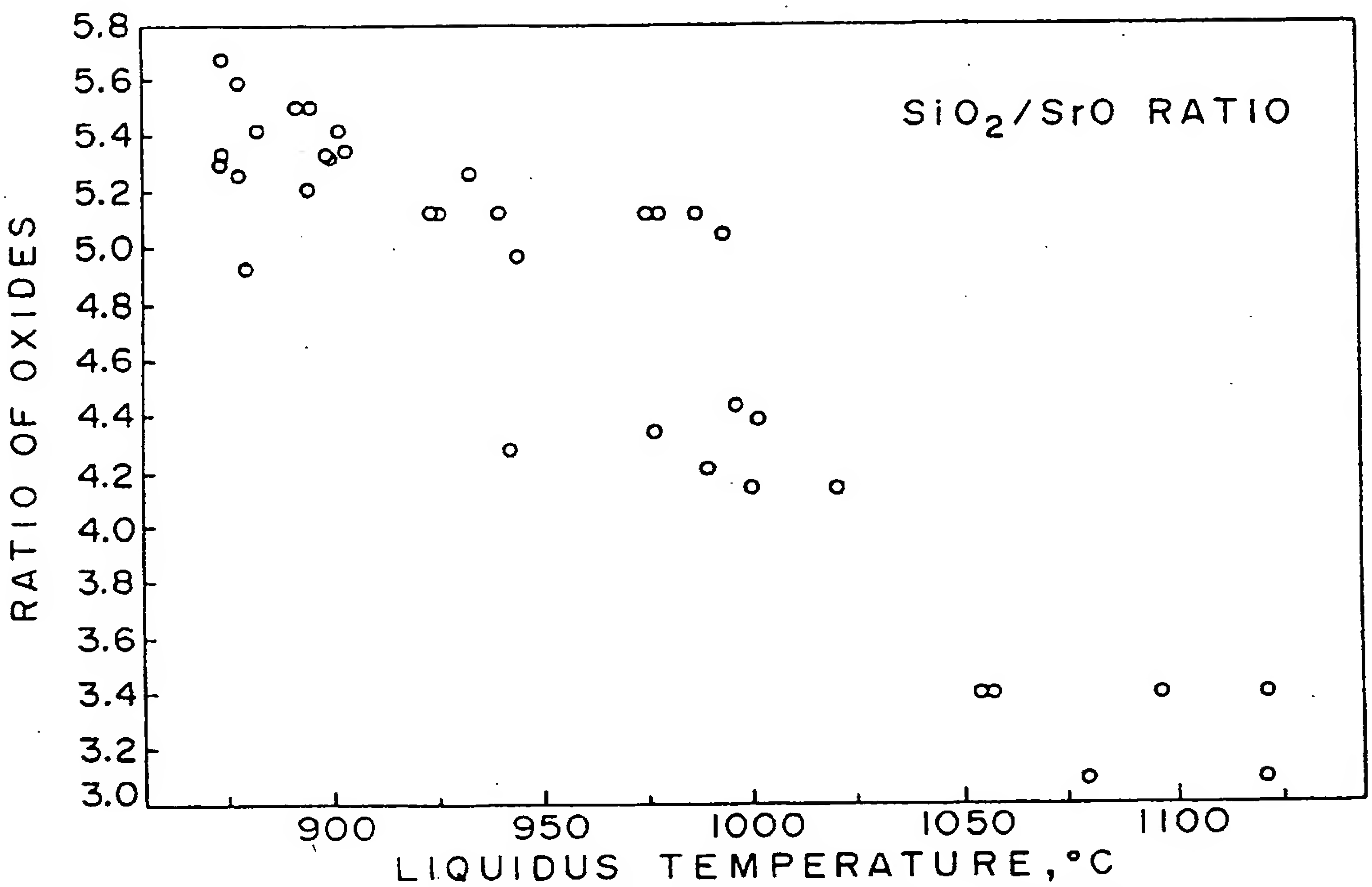


FIG. 5 - INCREASE SiO_2/SrO RATIO LOWERS LIQUIDUS

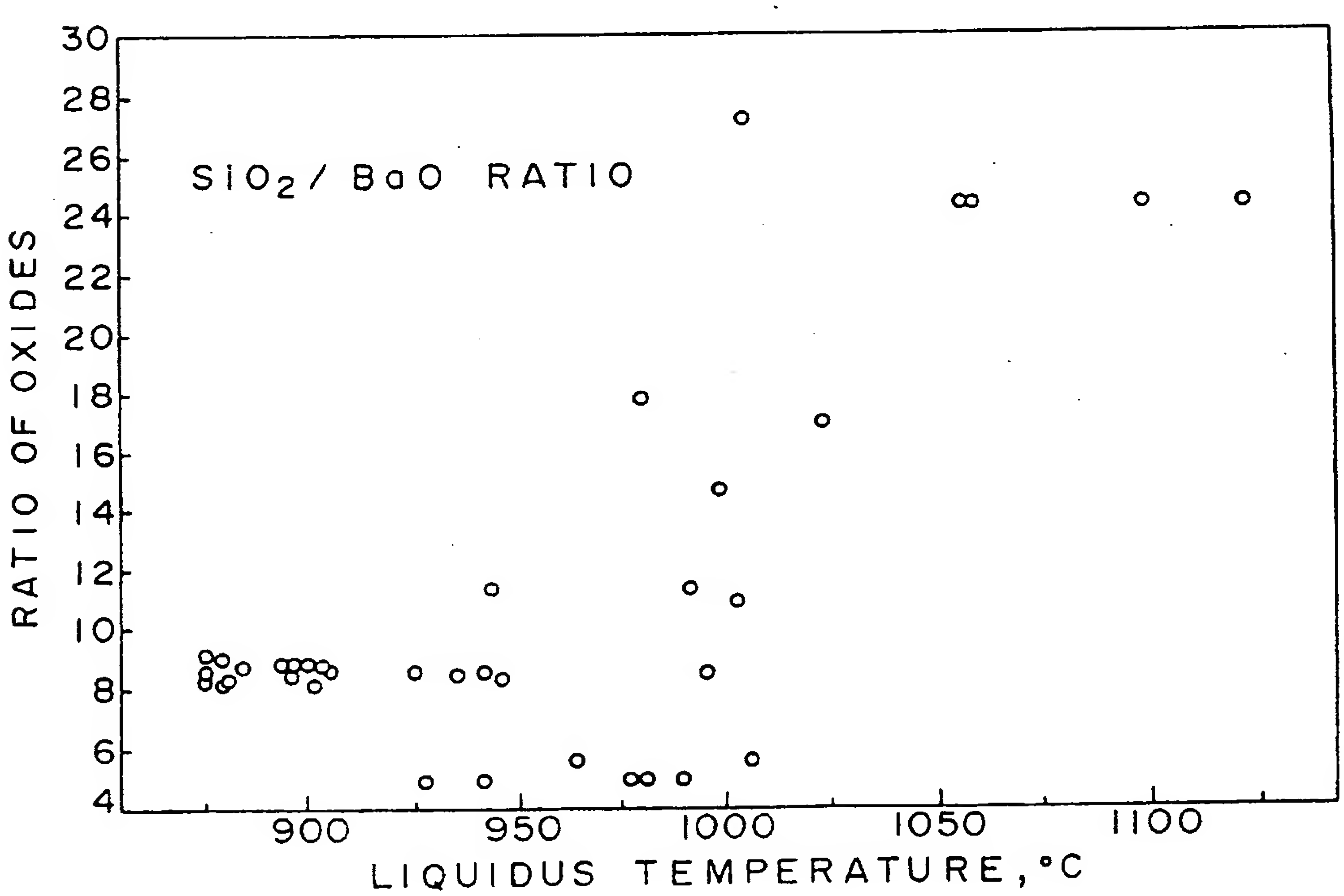


FIG. 6 - SiO_2/BaO RATIO BELOW 15; LOW LIQUIDUS

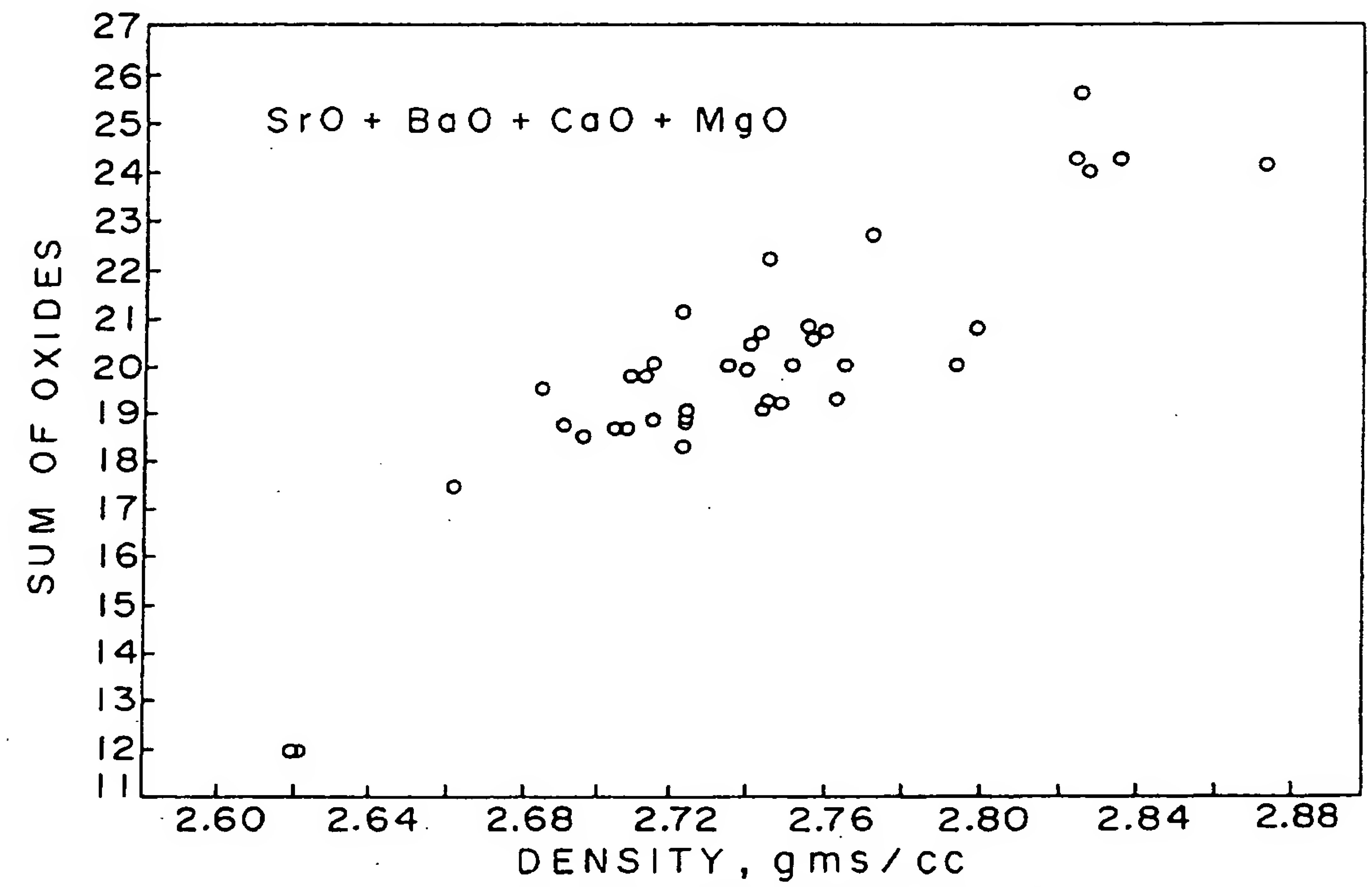


FIG. 7 - INCREASE ALKALINE EARTHS RAISES DENSITY

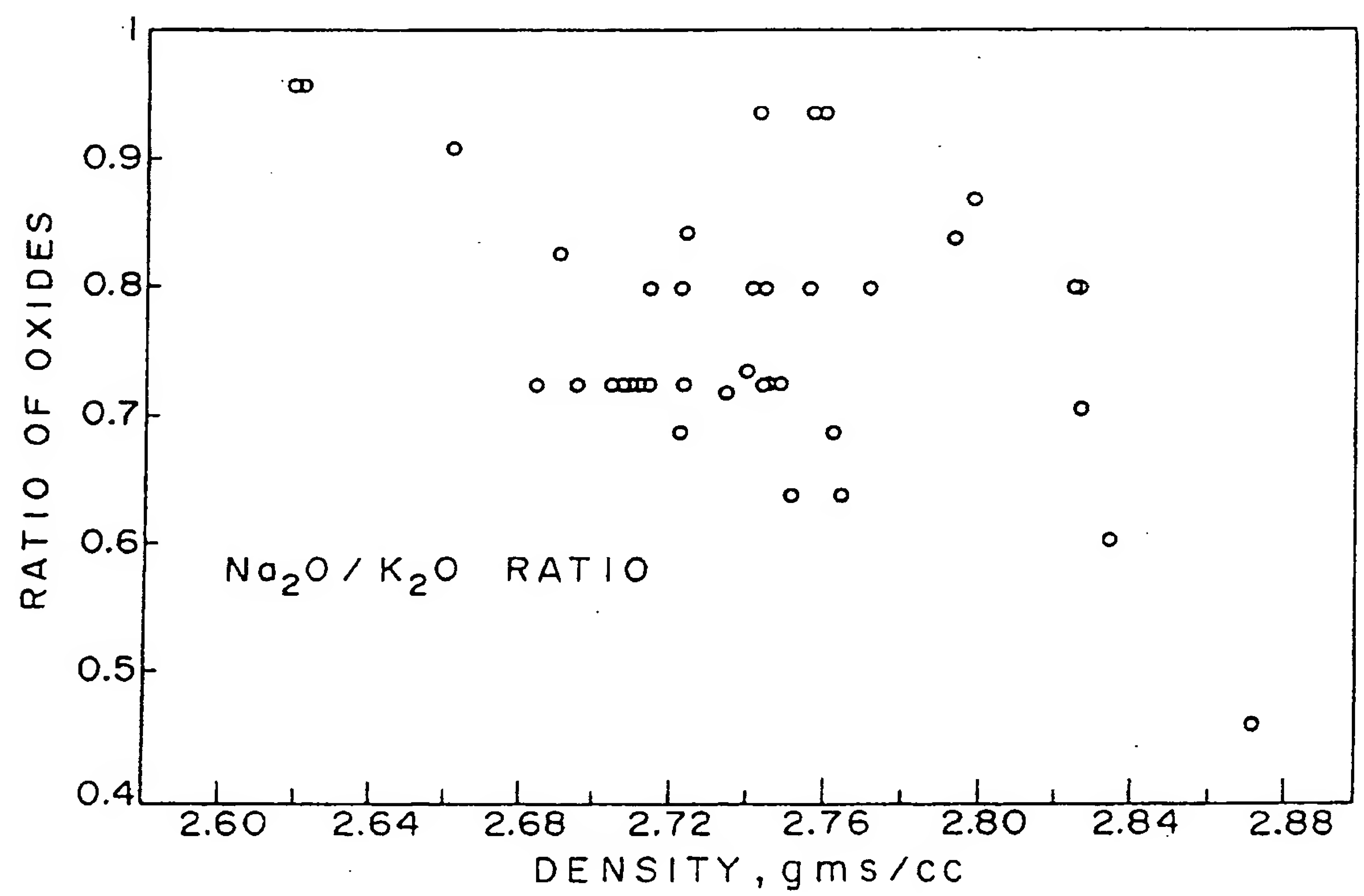
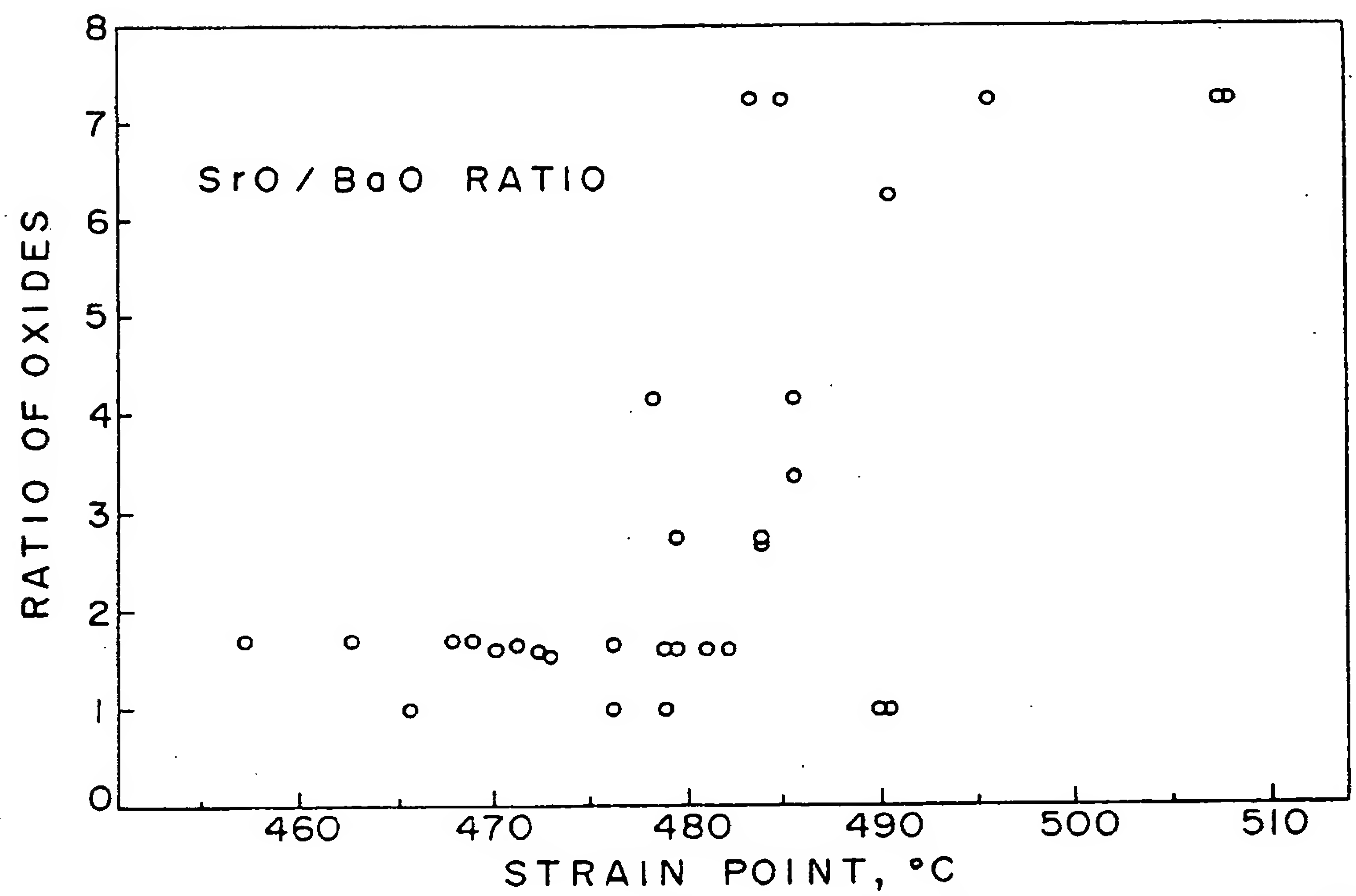


FIG. 8 - DECREASE Na_2O / K_2O RATIO RAISES DENSITY



DECREASE SrO / BaO RATIO LOWERS STRAIN POINT

FIG. 9

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 2301

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-2 021 505 (NV PHILIPS GLOEILAMPENFABRIEKEN) * claims *	1-19	C03C4/08 C03C3/095 H01J29/86
X	US-A-3 805 107 (BOYD) * column 3, line 44 - line 60 *	1-19	
X	DATABASE WPI Section Ch, Week 7602, 1976 Derwent Publications Ltd., London, GB; Class L, AN 76-02502X & JP-A-50 040 611 (ASAHI GLASS K.K.) 14 April 1975 * abstract *	1-19	
X	CHEMICAL ABSTRACTS, vol. 108, no. 14, April 1988, Columbus, Ohio, US; abstract no. 117540r, page 329 ; * abstract * & JP-A-62 288 134 (NIPPON ELECTRIC GLASS CO.) 15 December 1987	1-19	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 84, no. 20, 17 May 1976, Columbus, Ohio, US; abstract no. 143854b, page 590 ; * abstract * & JP-A-50 144 711 (ASAHI GLASS CO.)	1-19	C03C H01J
X	CHEMICAL ABSTRACTS, vol. 99, no. 22, 28 November 1983, Columbus, Ohio, US; abstract no. 180462c, page 286 ; * abstract * & JP-A-58 120 548 (ASAHI GLASS CO.) 18 July 1983	1-19	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 OCTOBER 1992	VAN BOMMEL L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 11 2301
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 99, no. 24, 12 December 1983, Columbus, Ohio, US; abstract no. 199544c, page 275 ; * abstract * & JP-A-58 120 537 (ASAHI GLASS CO.) 18 July 1983 ---	1-19	
X	DE-A-3 135 910 (NIPPON ELECTRIC GLASS CO.) * claims * -----	1-19	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 OCTOBER 1992	VAN BOMMEL L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document